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DEFECTS IN KCl CRYSTALS**

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A REVIEW ON THE PHOTOCHEMISTRY OF OH⁻ AND H⁻ DEFECTS IN KCl CRYSTALS¹

Spero Penha Morato² and Fritz Lüty³

ABSTRACT

A comprehensive investigation of the photodissociation of substitutional OH⁻ defects in KCl over a wide range of temperature, was reviewed including the study of the primary and secondary reaction products of this photodissociation. It was found that at LNT, the stability of the U₂ center (OH⁻ primary photoproduct) against optical bleaching is considerably higher than at LHeT. The same effect was observed in OH⁻ itself at RT. These low efficiency photodecomposition processes indicate efficient back processes that apparently recombines the photoproducts regenerating the original centers. The used KCl host material stands as a representative for the large family of cubic alkali halide crystals, while the OH⁻ ion represents other diatomic molecules of the type XH⁻ (like SH⁻), with supposedly similar properties. The observed phenomena and processes in KCl:OH⁻ may therefore be regarded as a model case for a large group of (crystal + defect) - systems.

1 - INTRODUCTION

Hydrogen defects are the most simple and fundamental chemical impurities in crystals which - due to their simple structure - are best accessible to a full quantum mechanical treatment of their properties and interactions with the surrounding lattice. Alkali halides crystals are specially attractive and informative for these studies as hydrogen hosts because substitutional or interstitial hydrogen can easily be identified by their transitions due to electronic and/or vibronic excitations.

Hydrogen ions (U centers) can be incorporated substitutionally^(1,2) in alkali halides. They produce a strong structureless electronic absorption band in the UV the maximum of which occurs at 214 nm for KCl and a narrow absorption line in the IR due to a strong localized vibration of the hydrogen ion (at 502 cm⁻¹ for KCl³) above the LO phonon frequencies of the lattice.

Low temperature UV light irradiation in the U band releases the H⁻ ion from its substitutional site to an interstitial position (U_i center) with an empty vacancy formed at the original site. This process is the low energy analog to the formation of the intrinsic charged Frenkel pair produced by high energy radiation in the pure crystal. Subsequent prolonged broad band irradiation in the UV will excite the U_i absorption of the H_i⁻ ion leading to its ionization and transfer of the electron back to the anion vacancy. These process can be represented by the following reactions:



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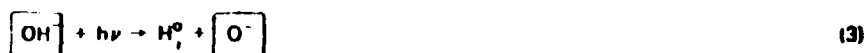
(2) Supported by FAPESP grants # 71/861 and 76/029 and CNEN. Now at the Instituto de Energia Atômica, C.P. 11049 - São Paulo, Brazil.

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by this process the extrinsic charged Frenkel pair is converted into a neutral pair consisting of an F center and an interstitial hydrogen atom (U_2 center). This latter defect is characterized by an electronic absorption band in the UV (at 236 nm in KCl).

Hydrogen defects can also be directly obtained from the low temperature photodecomposition of OH^- impurities⁽⁴⁾ which are incorporated substitutionally in alkali halides⁽⁵⁾. OH^- ions, the most simple heteronuclear diatomic lattice defect, give rise to electronic, vibrational and librational optical excitations. The electronic absorption consists of a broad structureless and asymmetric band in the UV (at 204 nm for KCl).

The excitation of the OH^- electronic transition produces the photodissociation of the OH^- ion. The primary products of this process, as initially proposed by Kerkoff⁽⁴⁾ consist of an interstitial hydrogen atom (H_i^0 center) and an oxygen ion left at the original OH^- lattice site. This photoreaction can be represented by the following equation:



In this present work we shall review the phenomenology of the photodissociation of OH^- defects in KCl over a wide range of temperatures including the study of the primary and secondary products of this photodissociation.

Special attention is focused on the low temperature thermal behaviour of the several photoproducts involved and their possible stabilization at higher temperatures if a suitable trap is provided. The next paper (part II ()) will present a detailed study on the formation and extinction kinetics of a new configuration of atomic charged hydrogen that is not connected to any other impurity.

2 - EXPERIMENTAL PROCEDURES

Most of the optical measurements, optical and thermal treatments were carried out with an He^{I} optical mald by F. X. Stohr (Germany). This cryostat was provided with four windows which permitted parallel and crossed optical beam experiments, together with the possibility of exchanging windows according to the specific spectral requirements of the experiment. A variable temperature tail for this cryostat was designed and built, based on the principle of exchange gas as a thermal switch⁽⁷⁾ controlled by thermocouples and thermistors. The sample holder was designed to meet the most variable requirements such as crossed or parallel optical beam geometries. It consisted of an L-shaped piece of copper machined out of a solid block. It was pressed against the bottom plate of the exchange gas chamber by a circular brass flange, with indium foils interposed between the mechanical parts to increase the thermal contact. In this way, quick changes of geometry were possible just by releasing the flange screws and rotating the sample holder. Soldered to the sample holder was a heater element. The high power dissipation characteristics of this heater were necessary in order to achieve quick temperature changes, different heating rates and high temperature annealings. The heater element was powered by a Variac transformer.

The KCl crystals were grown from the melt by the Kyropoulos method under a controlled argon gas atmosphere⁽⁸⁾, in the Utah crystal growth laboratory. The starting crystal material was ultrapure grade from E. Merck AG Darmstadt (Germany). Some ultrapure material was subject to a pretreatment with HCl at high temperatures to eliminate as much as possible traces of OH^- or oxygen impurities. In other crystals, KOH was intentionally added to the melt in controlled amounts in the range of 10^{-3} to 10^{-4} mole percent to dope the crystal with the desired OH^- content. The samples were cleaved from the middle of the block to avoid the (possibly contaminated) surface sections. Sample dimensions ranged from .30 to 10.0 mm thickness for the optical path according to the experimental

- requirements. The samples were mounted on the sample holder by compression with a spring-loaded copper frame.

For undispersed UV + visible light irradiations, we used a 150 W Xenon lamp from Hanovia 901C-11, mounted in a Bausch Lomb lamp housing and equipped with UV grade quartz condenser lens system. For monochromatic irradiations in the UV region we used the Xenon lamp mounting attached to a Bausch and Lomb grating monochromator. The band pass used was approximately 20 nm. In general, higher order spectra were not eliminated. When it was necessary to obtain a fairly pure monochromatic irradiation, two monochromators were coupled in a tandem arrangement. Optical absorption measurements were carried out with the Cary 14 or Beckman IR-12 recording double-beam spectrophotometers. The resolution obtained with the Cary 14 was around 1 nm. The resolution obtained with the Beckman IR-12 was variable, from 1 to 12 cm^{-1} according to the experimental requirements. The determination of concentration for the centers involved in this work was done by using the Smakula formula. For calculation of the OH^- concentration we used the calibration described by B. Fritz, et al⁽⁹⁾.

3 - RESULTS AND DISCUSSIONS

3.1 - Low Temperature Photochemistry

In our effort to study comprehensively the photodissociation of the OH^- defect in KCl, we covered the whole temperature range from liquid helium to room temperature and divided this temperature range into three intervals. The choice of these intervals was suggested by the thermal stability of the main reaction products of the OH^- photodissociation. The first and most important temperature interval to study the OH^- photodissociation is the one in which the H_i^0 center is thermally stable, that is below about 100K. Below 200 K we find other centers like H_i^+ thermally stable and this defined the upper limit of our second temperature interval. Above 200K, up to room temperature, apparently none of the products of the OH^- photodissociation is stable.

Like most of the alkali halides, the OH^- absorption in KCl is broad (halfwidth about 0.5 eV), structureless and asymmetric, and has an oscillator strength of about 0.13^(5,9). We photodissociated the OH^- defect in two different temperatures (LHeT and LNT) as displayed in Figure 1. By irradiation into the OH^- band we obtained its decrease accompanied by the increase of the other bands, due to the H_i^0 and the O^- centers which are the primary products of the OH^- photodissociation. Only the long wavelength tail of the O^- band could be measured due to spectral restrictions of the spectrophotometer. In these temperatures the OH^- photodissociation process showed a temperature independent quantum efficiency.

The electronic absorption of the H_i^0 center in KCl consists of a single band (U_2 band) peaking at 236 nm. Like the OH^- band for KCl, this band is structureless and asymmetric (halfwidth about 0.40 eV) and its oscillator strength is of the order of 0.33. Similar to the OH^- photodissociation process we obtain by irradiation at LHeT into the U_2 band, its decrease accompanied by the appearance of two other bands, the U band (H^- center) and the H band (Cl_i^0 crowdion). The photodissociation of the H_i^0 at LHeT is spectrally shown in Figure 2. The simultaneous creation of U and H bands strongly indicates that the hydrogen atom occupies the vacancy left by the halogen atom during the excitation. This process can be represented by the following equation:



The H_i^0 centers generated by the photodissociation of OH^- defects are isolated and unperturbed interstitial hydrogen atoms which have been extensively studied by EPR and ENDOR techniques in several alkali halides^(10,11,12,13) (see Figure 3A). H_i^0 centers can also be produced either by irradiation into U_2 band of H_i^0 defects⁽¹⁴⁾ or by the photodissociation of any molecule of the form XH^- (like

SH^(15,16), X standing for an element of group VI. In a model proposed by Kerkoff, et al⁽¹⁷⁾, the H_i⁰ center can be described by a tetrahedral HCl₄⁻ molecular ion in which one positive hole in its ground state is mainly bound to the interstitial hydrogen atom (Figure 3A). This ground state hole gives rise to a spin resonance. In the U₂ band optical transition to the excited state, a charge transfer mechanism brings one electron of the four surrounding chlorine ions into the hydrogen atom (Figure 3B). Therefore the unrelaxed excited state of the H_i⁰ center will correspond to a configuration where the hole is more bound to the four surrounding halogen ions and consequently less localized (Figure 3B). Kurz⁽¹⁸⁾ suggested that in this excited state the lattice will undergo a non-cubic relaxation process (static Jahn-Teller distortion, Figure 3C) after the H_i⁰ center excitation takes place. This non-cubic lattice relaxation will lower the symmetry possibly displacing the hydrogen ion in the <100> direction and moving chlorine ions in the <100> directions. A polarization of the charge distribution will also take place changing the potential experienced by the hydrogen. The hole will tend to become more localized at the two chlorine ions which approach each other. Annihilation between the transferred electron and the hole may occur restoring the original H_i⁰ center configuration. Experimentally, however, one observes the H_i⁰ center photodestruction (with a quantum efficiency which is not yet determined quantitatively). This fact will require some finite escape probability for one of the Cl atoms. Its vacancy will be occupied by the hydrogen ion forming a H⁻ center. The halogen atom will escape in a <110> collision replacement sequence until it is well separated from the vacancy (hydrogen) left behind and stabilized as a Cl_i⁰ crowdion (H band), as seen in Figure 3D.

A more quantitative approach to the H_i⁰ photodestruction leads us to Figure 4A where we show the changes in the height of the U₂, H and U bands as a function of the monochromatic U₂ band light irradiation at 6K. Plotting the formed reaction products (H⁻ and Cl_i⁰ centers) against the destroyed H_i⁰ centers, we obtain straight lines (Figure 4B). This is consistent with the assumption that the H_i⁰ centers decomposition proceeds in a one-to-one ratio to form both H⁻ and Cl_i⁰ centers (Eq. 4). In this picture, the differences in slope are due to differences in oscillator strengths and halfwidths of the two bands. From these slopes the relative oscillator strengths of the U₂, U and H absorptions can be determined.

From the thermal destruction of all Cl_i⁰ crowdions (monitored by the complete extinction of the H band), we observed that the process described by Eq. 4 has not been completely reversed. This is clearly shown in Figure 2 which contains the final balance between U and U₂ bands after the complete H center destruction by annealing to 77K was made Figure 2. Considering the ratio between the amounts of H⁻ defects consumed in this back process and the amount of H_i⁰ centers returned, we get the same value obtained in the production process described by Eq. 4. This indicates that apparently no H⁻ or H_i⁰ centers were involved in other reactions during the annealing procedure. Nevertheless, the ratio between Cl_i⁰ crowdions consumed and H_i⁰ centers returned is much higher than in the crowdion production process indicating that part of the Cl_i⁰ crowdions during thermal annealing did not make this same back process but must have been trapped and stabilized somewhere else in some other form. However, no new absorptions were observed to develop in the whole UV and visible region of the spectrum. The question, into what structures the mobile Cl_i⁰ crowdions become trapped and stabilized, remains open and unanswered at this point.

Irradiation into the U₂ band at LNT leads to spectral changes very similar to the ones obtained in the above discussed case of LHeT irradiation: The U₂ band is reduced and the U band is formed (Figure 5). No H band is formed as expected from the fact that the Cl_i⁰ crowdions are no longer stable at LNT. If we plot - similarly as for the LHeT case in Figure 4 - the U₂ and U band changes against irradiation time (Figure 6A) and compare the increase of the U band with the U₂ band decrease (Figure 6B) we find, in comparison to the LHeT behavior, the following changes:

- a) The initial quantum efficiency for the optical H_i⁰ center destruction is about ten times smaller than it was at LHeT (Figure 6A).
- b) Though a linear relation between U₂ band decrease and U band increase is again obtained (Figure 6B), their ratio is different from the one obtained at LHeT.

Phenomenologically (a) shows that the stability of the H_i^0 center against optical bleaching is considerably higher than at LHeT. If we assume that the initial photodestruction of the H_i^0 center produces the Cl_i^0 crowdion center (as it does at LHeT), this thermally unstable interstitial center may easily recombine back and restore the initial H_i^0 center. This would account for the low efficiency of the H_i^0 center photodestruction.

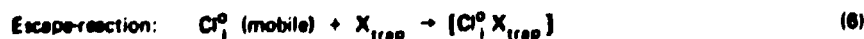
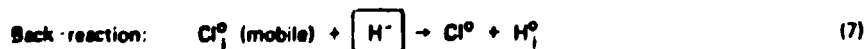
Still in 10% of the U_2 band excitation cases (compared to LHeT), the H_i^0 photodestruction works and U centers are formed. This means that the mobile Cl_i^0 crowdion did escape without recombination and must get trapped and stabilized at some unknown place, undetectable with UV and visible spectroscopy. The fact that in this process the $|\Delta U| : |\Delta U_2|$ ratio is different from the 1:1 ratio found at LHeT as indicated in (b) suggests that hydrogen in some form may be involved in the stabilization and trapping of the Cl_i^0 crowdion.

The precondition for this line of arguing is the assumption that the photoexcitation of the H_i^0 center at LNT leads – similarly to the LHeT case – primarily and initially to the formation of a Cl_i^0 crowdion – even if it is thermally not stable and therefore not detectable by the H-band. This assumption was experimentally proved by simply offering the Cl_i^0 crowdions a trap would thermally stabilize them. This was achieved by additionally introducing Na^+ impurities in the $KCl:OH^-$ system. Cl_i^0 centers trapped in the immediate vicinity of a simple substitutional Na^+ impurity are the so called H_A centers⁽¹⁹⁾.

H_A centers in KCl give rise to a strong transition at 357 nm and a weaker one at 560 nm. These H_A bands have a thermal decay temperature of about 113K. We repeated with $KCl:Na^+ + OH^-$ crystal at 77K the same previously described sequence of monochromatic irradiations starting with the OH^- photodissociation, followed by the U_2 band photodestruction. The results are displayed in Figure 7. As we can see from there, we were able to produce H centers and have them trapped at Na^+ impurities and stabilized at 77K. This process can be described by the following equation:



These experiments show clearly that photoexcitation of H_i^0 centers at LNT leads (similar to the LHeT case) to the production of Cl_i^0 crowdions. The difference to the low temperature case is that these crowdions are thermally unstable and mobile (i.e., don't appear by the H band absorption). They either recombine with the U center and restore the initial H_i^0 defect, or escape in the lattice looking for a different trapping site. In a Na^+ doped crystal they can be trapped by a Na^+ ion, forming the thermally stable H_A (Na^+) configuration. We can therefore conclude that in our crystal with oxygen and various hydrogen defects a different trapping place is operative, which can stabilize the mobile Cl_i^0 crowdion and therefore allow even at LNT the $H_i^0 \rightarrow H^-$ conversion. Thus we must have at LNT reactions of the type:



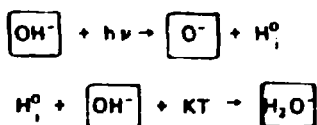
The same X_{trap} would have been responsible for the unaccounted disappearance of Cl_i^0 crowdions in the thermal annealing process after their production at LHeT, treated before. In both cases, no UV or visible absorption has been found to identify the $[Cl_i^0 X_{trap}]$ complex. As hydrogen in some form is a strong candidate for the X_{trap} , we set up IR experiments with the aim to possibly

identify the trapped Cl_i^0 crowdion by local mode spectroscopy. This subject will be treated in the next paper (Part II).

3.2 - Photodecomposition of OH^- above 120K

We next investigated the OH^- photodecomposition at temperatures above the thermal stability of the H_i^0 center. By irradiating into the OH^- band at 150 K, we obtained its decrease accompanied by the increase of the H_2O^- band⁽²⁰⁾. This process is displayed in Figure 8. Plotting in a manner similar to the low temperature case, the OH^- and H_2O^- band changes vs. irradiation time (Figure 9A), and comparing the increase of the H_2O^- band with the OH^- band decrease (Figure 9B), we find that following results: a) compared to the LNT or LHeT OH^- photodecomposition, we observed that the initial quantum efficiency of OH^- destruction at 150K is a factor of two higher than it was at LNT or LHeT; b) by plotting the OH^- absorption band decrease vs. H_2O^- absorption band increase, a linear relation between the OH^- decrease and H_2O^- increase is obtained (Figure 9B), indicating a direct conversion process between centers without other side reactions.

The factor of two obtained between the OH^- destruction rates at LNT or LHeT and 150K suggests that for each H_2O^- center formed two OH^- centers were consumed - one by photodestruction process, and the other by trapping a mobile H_i^0 center. These observations suggested the following set of equations:



Adding these two equations, we obtain:



At higher temperatures (especially at RT) it is very hard - if not impossible - to control all the process that are taking place simultaneously due to the instability and consequent mobility and aggregation of the different centers involved. Processes like interstitial molecules and colloid formations are usually the end products of high temperature photochemistry. To get an idea of how a pure $\text{KCl}:\text{OH}^-$ system would behave under OH^- high irradiation at RT, we basically repeated the experiments already done at lower temperatures and observed that very little changes occurred. We obtained a slight shift to lower energies (≈ 25 nm) in the original OH^- band in the UV region, possibly due to a very small amount of U-band development, and a very small build-up of an F band. These results clearly show a high stability of the OH^- defect against optical bleaching at these high temperatures. As none of the primary and secondary reaction products treated at low temperatures (H_i^0 , H_i^- , Cl_i^0 , H_2O^-) remain stable (or lack of stable trapping partners) at this high temperatures, an efficient back-process apparently regenerates the OH^- center after its photo-dissociation.

RESUMO

Uma investigação abrangente sobre a fotodissociação de defeitos substitucionais OH^- em KCl foi revista para uma extensa região de temperaturas, incluindo o estudo dos produtos primário e secundário resultantes desta fotodissociação. Foi encontrado que a estabilidade do centro U_2 (produto primário da dissociação do OH^-), sob irradiação UV à temperatura de N_2 líquido é consideravelmente maior que a temperatura de He líquido. O mesmo efeito foi observado com o íon OH^- à temperatura ambiente. Este processo de fotodissociação de baixa eficiência indica um processo reversível de alta eficiência que aparentemente recombina os produtos de fotodissociação regenerando o centro original. A matriz KCl utilizada neste caso é tida como a de representantes da família de cristais cúbicos de haletos alcalinos, enquanto que o íon OH^- representa moléculas diatômicas do tipo XH^- (como SH^-) com propriedades similares. Os fenômenos e processos observados em KCl:OH^- podem desta forma ser interpretados como caso modelo para um extenso grupo de sistemas (cristais e defeitos).

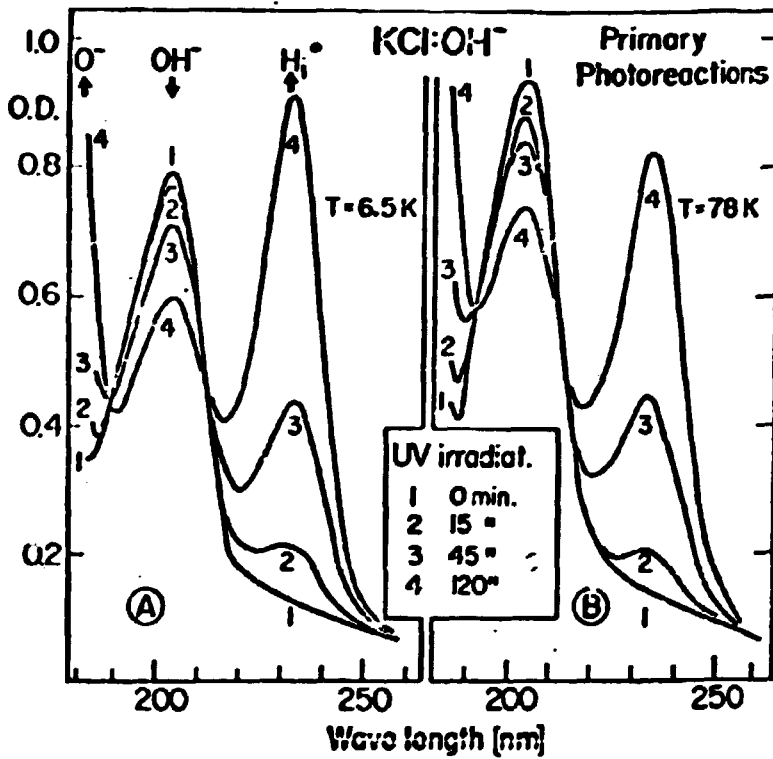


Figure 1 - Optical absorption spectra of a KCl:OH⁻ crystal showing the primary products of OH⁻ photodecomposition under OH⁻ light (204 nm) after different irradiation times at 6.5K (A) and 78 K (B).

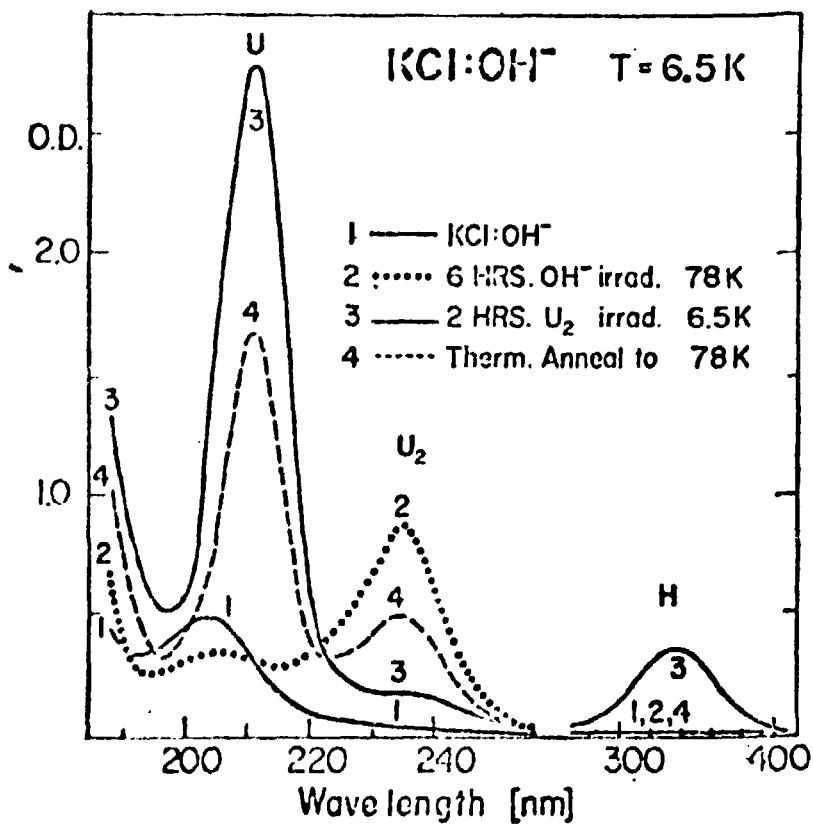


Figure 2 -- U₂ center photodestruction spectra at 6.5K and subsequent pulse anneal to 77K, measured at 6.5K.

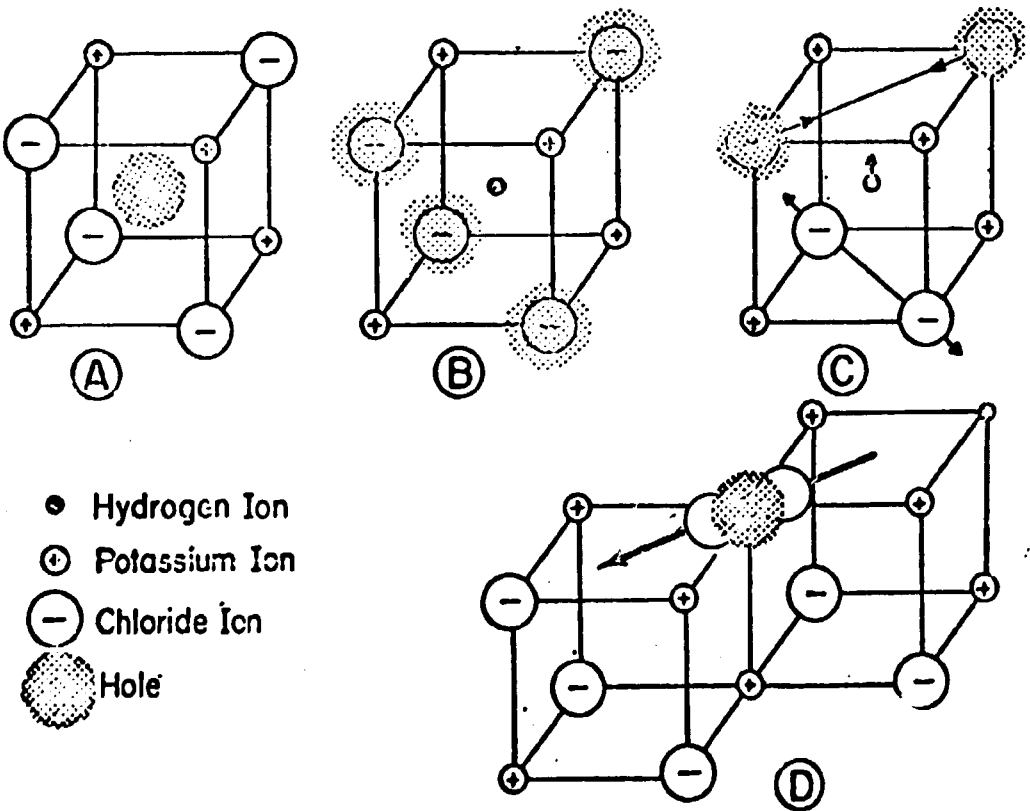


Figure 3 - A. H_0^0 center ground state (the hole is bound to the H^- ion).
B. H_0^0 center unrelaxed excited state after the charge transfer (the hole is shared equally by the four Cl^- ions).
C. Lattice relaxation and the Jahn-Teller distortion (the hole becomes more localized at the two Cl^- ions which approach each other).
D. Formation of an H^- center with the creation of a Cl_0^0 crowdion moving in a $\langle 110 \rangle$ replacement sequence.

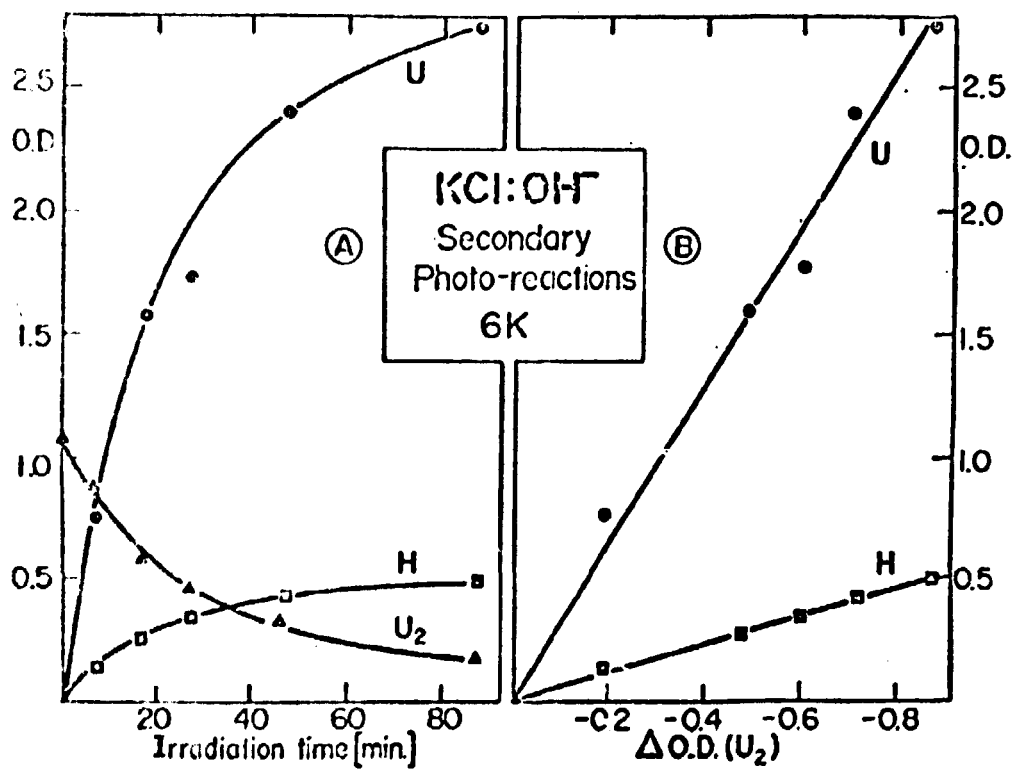


Figure 4 -- Photodecomposition of U₂ centers at 6K.

- A. Decrease of the U₂-band absorption and increase of the U- and H-band absorption as a function of irradiation time (monochromatic 235 nm light).
- B. The U- and H band increase plotted as a function of the U₂-band decrease, yielding linear correlations.

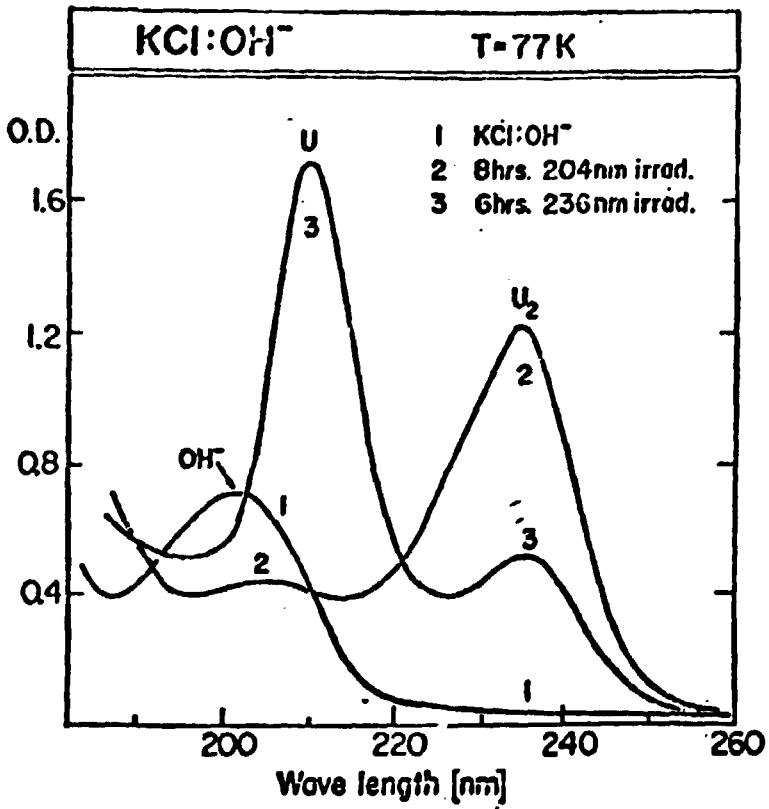


Fig. no 5 - Photo-dissociation of OH⁻ centers (1 → 2) and subsequent H⁰_i center photodestruction (2 → 3), at 77K.

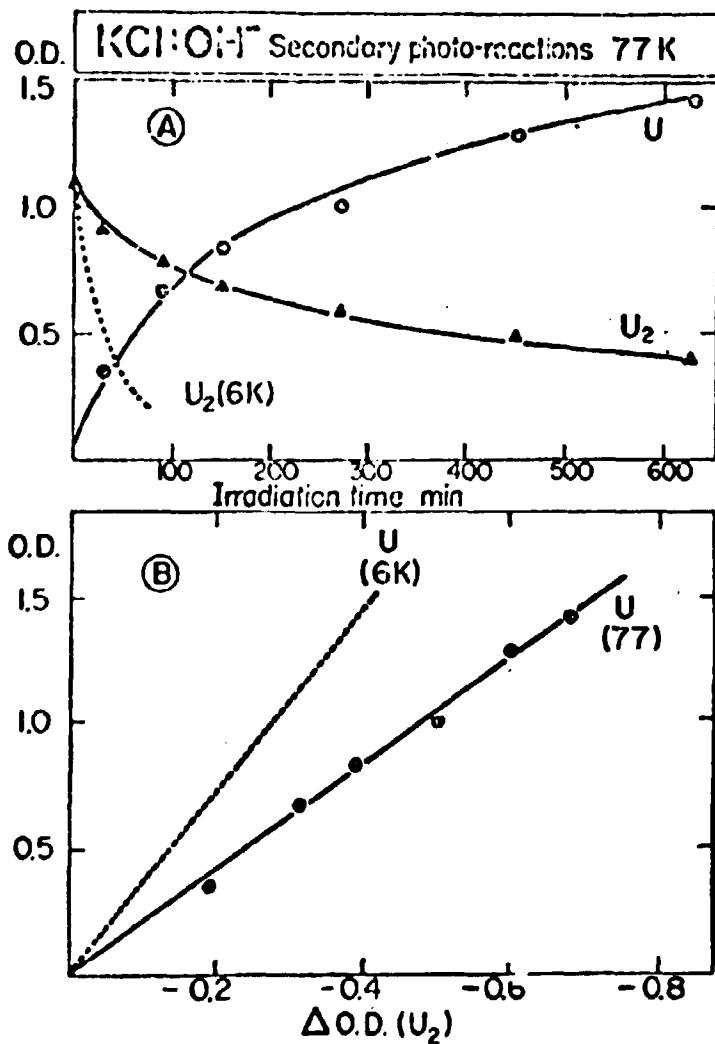


Figure 6 - Photodecomposition of U_2 centers at 77K.

- A. Decrease of the U_2 band absorption and increase of the U band absorption. The dashed line indicates the initial rate obtained at 6K.
- B. The U band increase plotted as a function of the U_2 band decrease. The dashed line indicates the same reaction at 6K, corrected for the broadening effect on the perturbed H^+ centers.

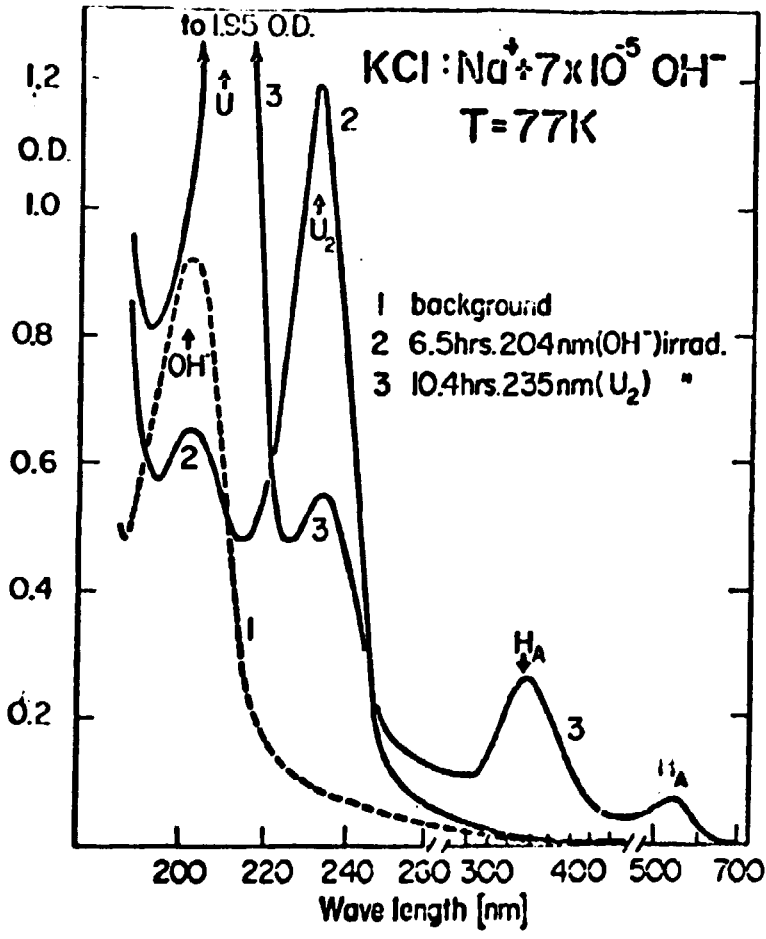


Figure 7 - H_A center formation in a KCl:OH⁻ + Na⁺ crystal under U₂ light irradiation at L.T.

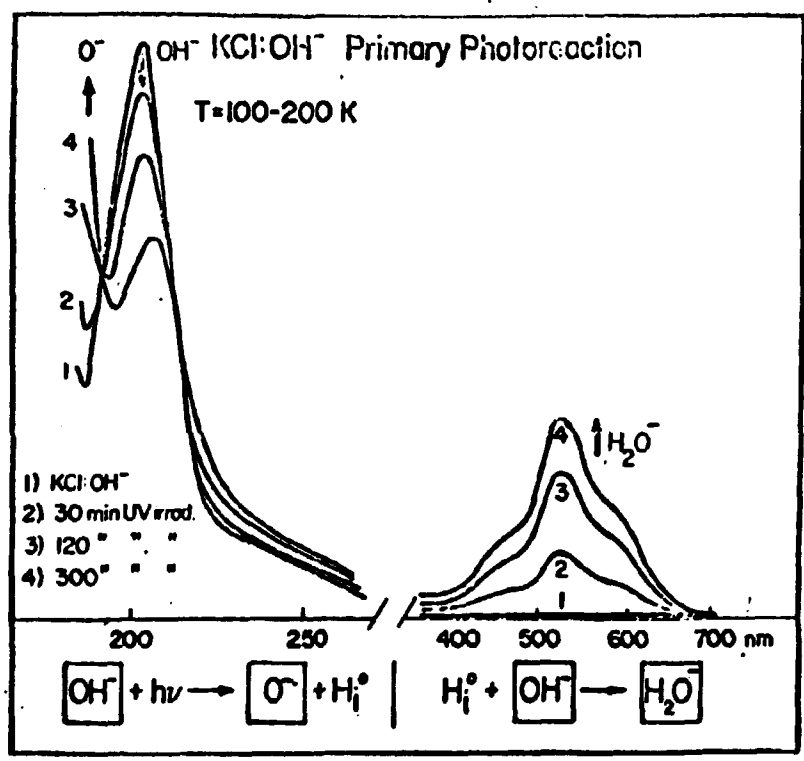


Figure 8 - Optical absorption spectra of a KCl:OH⁻ crystal, measured at 77K, showing the direct secondary product formation of the H₂O⁻ light irradiation.

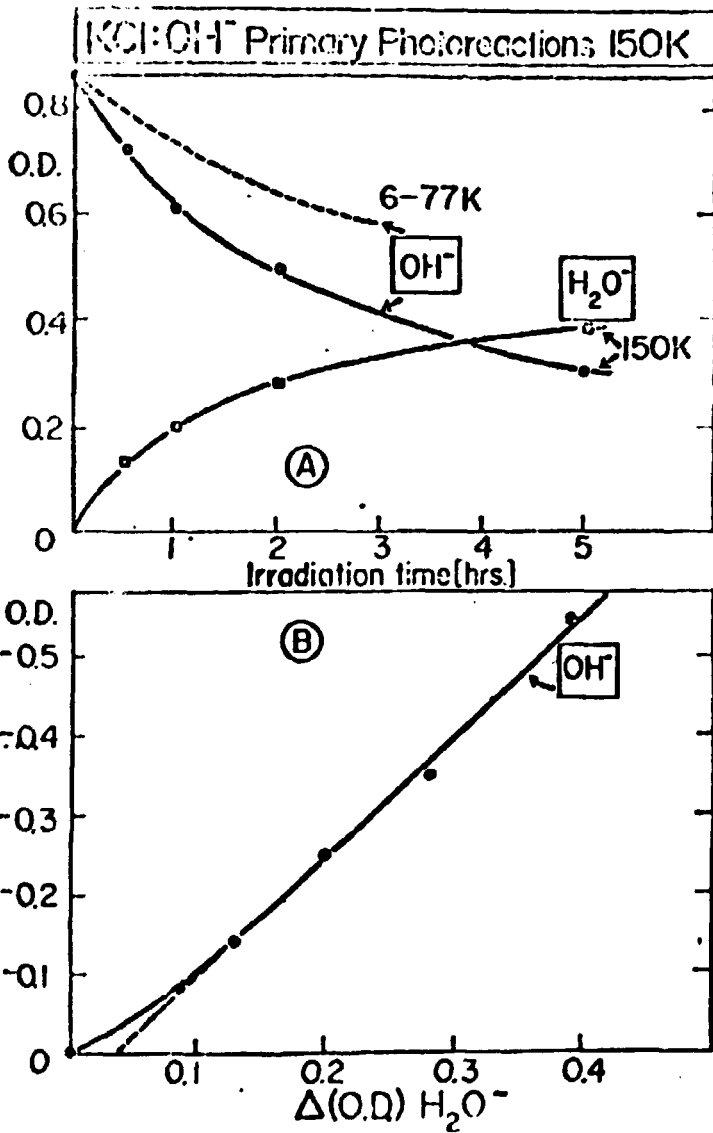


Figure B A. Direct secondary photo and thermal reaction rates at 150K. The dashed line indicates the OH⁻ band decay rate at 77K (measurements at 77K).
 B. Respective linear correlations observed between OH⁻ absorption band decrease and H₂O⁻ absorption band increase.

REFERENCES

1. R. W. Pohl, Proc. Phys. Soc. 49, 3 (1937).
2. R. Hilsch and R. W. Pohl, Trans. Faraday Soc. 34, 883 (1938).
3. G. Schaefer, J. Phys. Chem. Solids 12, 233 (1960).
4. F. Kerkoff, A. Physik 158, 595 (1960).
5. H. Paus and F. Lüty, Phys. Stat. Sol. 12, 341 (1965).
6. S. P. Morato and F. Lüty, Publicação IEA 507.
7. G. K. White, *Experimental Techniques in Low Temperature Physics*, 2nd ed., Oxford (1968).
8. F. Roseberger, Mat. Res. Bull. 1, 55 (1966).
9. B. Fritz, F. Lüty, and J. Anger, Z. Physik 174, 240 (1963).
10. J. M. Speath and M. Storrn, Phys. Stat. Sol. 42, 739 (1970).
11. J. M. Speath and H. Seidel, Phys. Stat. Sol. 46, 323 (1971).
12. G. Reuter, L. Schwan and J. M. Speath, Phys. Stat. Sol. (b) 53, K29 (1972).
13. M. H. Wagner and J. M. Speath, Solid State Comm. 14, 1101 (1974).
14. C. J. Delbecq, B. Smaller and P. H. Yuster, Phys. Rev. 104, 599 (1956).
15. F. Fischer and H. Gründig, Z. Physik 184, 299 (1965).
16. J. Rolfe, Appl. Phys. Letters 6, 66 (1965).
17. F. Kerkoff, W. Martienssen and W. Sander, Z. Physik 173, 184 (1963).
18. G. Kurz, Phys. Stat. Sol. 31, 93 (1969).
19. C. J. Delbecq, D. Hutchinson, D. Schoemaker, E. L. Yasitis and P. H. Yuster, Phys. Rev. 187, 1103 (1969).
20. W. Rusch and H. Seidel, Solid State Comm. 9, 231 (1971).

